

On the origin of biquadratic exchange in spin 1 chains

Frederic Mila¹ and Fu-Chun Zhang²

¹ *Laboratoire de Physique Quantique, Université Paul Sabatier, 31062 Toulouse Cedex, France*

² *Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221*

One dimensional spin 1 systems may have a rich phase diagram including Haldane gap and dimerized phases if the usually very small biquadratic exchange becomes significant. We show that this unlikely condition may be fulfilled in electron systems with quasi-degenerate orbitals. This mechanism may have been experimentally realized in the spin 1 chain LiVGe_2O_6 . The implications for the exploration of the physics and quantum chemistry of spin 1 chains are discussed.

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There has been a lot of activity recently on the physics of one-dimensional (1D) spin 1 systems, especially after the prediction by Haldane that the 1D Heisenberg model has a spin gap for integer spins [1]. That prediction has been confirmed since then by the observation of a gap in many spin 1 chains [2]. There has also been a lot of progress in the study of the most general Hamiltonian describing an isotropic coupling between neighboring spins 1, namely [3]

$$H = \sum_{\langle ij \rangle} H_{ij},$$

$$H_{ij} = J_1 \vec{S}_i \cdot \vec{S}_j + J_2 (\vec{S}_i \cdot \vec{S}_j)^2, \quad (1)$$

where the sum $\langle ij \rangle$ is over nearest-neighbor pairs. The phase diagram of this model is extremely rich [4]. It is most easily described using the parametrization $J_1 = J \cos \theta$, $J_2 = J \sin \theta$. As illustrated in Fig. 1, the system has two gapped phases: The Haldane phase for $-\pi/4 < \theta < \pi/4$ and a dimerized phase for $-\pi/4 < \theta < -\pi/4$. The two phases are connected by a critical point at $\theta = -\pi/4$ for which the model is exactly solvable and the spectrum is gapless. In addition, there is a Lifshitz point and a disordered point in the Haldane phase, as well as a Valence Bond Solid point [3], and the properties for $\pi/4 < \theta < \pi/2$ and $\theta \simeq -\pi/4$ are not totally agreed upon yet.

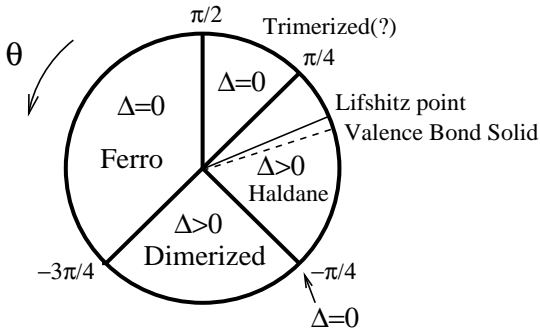


FIG. 1. Phase diagram of the general spin 1 model of Eq. (1) after Ref. [2].

Hopelessly, it has not been possible until very recently to explore this phase diagram experimentally due to the lack of systems with a sizable biquadratic exchange, which is conveniently measured by the ratio $-\beta = J_2/J_1 = \tan \theta$. It has been generally assumed that β is always small so that the system is always in the Haldane gap phase. The experiments on many spin 1 chain compounds have indeed supported this view until a very recent experiment on the 1D, spin 1 vanadium oxide LiVGe_2O_6 . In that experiment, an abrupt drop in magnetic susceptibility typical of a spin-Peierls transition has been observed at a temperature of 22 K [5]. This property is consistent with a gapless spectrum above this temperature, and it has been argued that this behavior is most likely due to the presence of a significant biquadratic exchange interaction [5].

Although biquadratic or higher-order spin exchange interactions have been discussed in the past and shown to induce anomalous magnetic properties in spin $S \geq 1$ systems, they are usually small [6,7]. It is therefore of interest to study the underlying mechanism for predominant biquadratic interaction.

In this paper we propose a new microscopic mechanism leading to a significant biquadratic interaction in spin 1 systems. We use a microscopic model to derive the interaction couplings J_1 and J_2 in Eq. (1) based on a perturbation theory, which is compared with exact numerical calculations. The key in our model is to include a third atomic orbital for an electron with slightly higher energy than the two singly occupied lowest orbital states, i.e. to consider the situation where we have a quasi-degeneracy of the orbitals on one site. The virtual electron transition via the third orbital level favors ferromagnetic spin interaction, which may compensate largely the antiferromagnetic superexchange interaction, leading to the predominance of the biquadratic interaction with $\beta > 1$. We believe that this mechanism may be relevant to LiVGe_2O_6 . In that case the three orbitals come from the t_{2g} orbitals of the vanadium ions, and the degeneracy is lifted due to a small distortion of the octahedra around the vanadium atoms [5]. More generally, we believe that

the exchange Hamiltonian is likely to have higher order contributions whenever the degeneracy between the last occupied and first empty orbitals is only slightly lifted. This situation could be realized in some other transition metal oxides.

Let us consider a lattice of atoms with two outer electrons per atom. The atomic orbitals of the lowest energy level is two-fold degenerate, labelled by indices 1 and 2. There is a nearby level of orbital 3, whose energy is higher by an amount of Δ . We focus on the electron interactions at the same atom, and denote by U ($U' < U$) the direct Coulomb repulsion between two electrons in the same (different) orbitals, and by $J_H > 0$ the exchange interaction. The exchange interaction favors a total spin 1 state for two electrons on each atom, where orbitals 1 and 2 are both singly occupied with parallel spins, and orbital 3 is empty. This is in accordance with Hund's rule. The effective spin-spin coupling arises when the electron has a virtual transition to the neighboring atoms. Let t_{lm} be the electron hopping integral from orbital l at site i to orbital m at site j with the electron spin conserved. If the hopping integral is small compared with U' , J_H and Δ , only virtual transitions are possible, and their net effect is to induce an intersite spin-spin coupling.

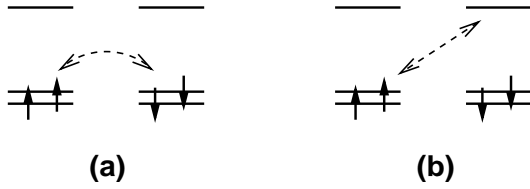


FIG. 2. Typical second-order exchange processes leading to: a) Antiferromagnetic bilinear exchange; b) Ferromagnetic bilinear exchange.

The spin Hamiltonian H_{ij} is uniquely determined by the total spin of two neighboring sites i and j . Let E_S the energy of the two-site system with total spin S , with $S = 0, 1$ or 2 . Then $J_1 = \frac{1}{2}(E_2 - E_1)$, and $J_2 = \frac{E_0}{3} + \frac{E_2}{6} - \frac{E_1}{2}$. Treating the hopping integrals as small parameters, the energy E_S can be calculated within perturbation theory. To illustrate the essential physics, we consider the simple case where $t_{11} = t_{12} = t_{13} = 0$, and $t_{22} = t_{33}$. To second order in the hopping integrals, and in units of t_{22}^2/U' , the spin couplings are given by [8]

$$\begin{aligned} J_1^{(2)} &= \frac{1}{2}(a_2 + a_3) - \frac{2}{3}\alpha^2(a_1 - a_2), \\ J_2^{(2)} &= 0, \end{aligned} \quad (2)$$

where $\alpha = t_{23}/t_{22}$, and the a 's are related to the Hund's couplings: $a_1 = (1 - j_H)^{-1}$, $a_2 = (1 + 2j_H)^{-1}$, $a_3 = (1 + 4j_H)^{-1}$, with $j_H = J_H/U'$. From Eqn. (2), we see that the biquadratic interaction vanishes in the second order of perturbation. This explains the smallness of the biquadratic coupling in most systems. The first term in $J_1^{(2)}$ arises from hopping to an occupied orbital

of the neighbouring site (see Fig. 2a) and corresponds to superexchange interaction. It is positive and favors antiferromagnetic alignment of the two spins. The second term arises from the virtual transition via the orbital state 3 (see Fig. 2b). Since $a_1 > a_2$, the contribution to J_1 is negative and it favors ferromagnetic alignment of the spins. Typical virtual transitions for the first and the second terms in J_1 are illustrated in Fig. 2. These two exchange mechanisms may compensate each other, leading to a very small net value of J_1 . In this situation, it is necessary to extend the perturbation to include the contributions from the fourth order terms. Since $\Delta \ll U'$, J_H , the most important contribution arises from processes involving a virtual state of spin 1 on both sites and with one electron in the excited state of orbital 3. Such a process gives an energy correction to the second order results by a ratio of order of $\delta = t^2/U'\Delta$. In Fig. 3 we show a typical example of such processes. All the other fourth order contributions are smaller by a factor of Δ/J_H or Δ/U' , and will be neglected in the present consideration.

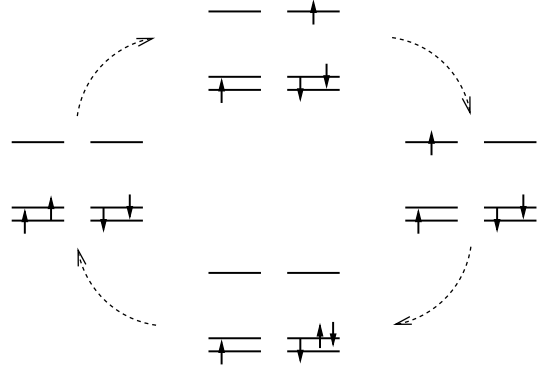


FIG. 3. Typical fourth-order process leading to a biquadratic interaction.

Summing over these fourth order terms, we find

$$\begin{aligned} J_1^{(4)} &= \delta[b_2^2 - b_1^2 + (b_3 + \frac{b_1}{3})^2], \\ J_2^{(4)} &= -\frac{\delta}{2}[b_2^2 + (b_3 - \frac{2}{3}b_1)^2], \end{aligned} \quad (3)$$

where $b_1 = \alpha^2 a_1$, $b_2 = \alpha(a_2 + a_3)$, and $b_3 = (a_2 - a_3)/2 - \alpha^2 a_2/3$. The correction to J_1 is simply an energy shift, which modifies slightly the location of the transition between ferromagnetic and antiferromagnetic bilinear interaction. The biquadratic interaction first appears in the fourth order in perturbation theory. While the ratio β is usually small, of the order of δ , it can be significant if the two contributions in the second order balance out and if Δ is relatively small. From equation (3), we also note that $J_2 < 0$, which suggests such a system is always in the lower half plane of the phase diagram in Fig. 1. This also implies $\beta > 0$ if $J_1 > 0$, and $\beta < 0$ if $J_1 < 0$. In Fig. 4b, we plot the value of β as a function of α for given Δ and J_H/U' . At $\alpha < 0.5$, β is vanishingly small. As

α increases, β increases sharply, and the divergent point corresponds to the transition from antiferromagnetic to ferromagnetic bilinear interaction.

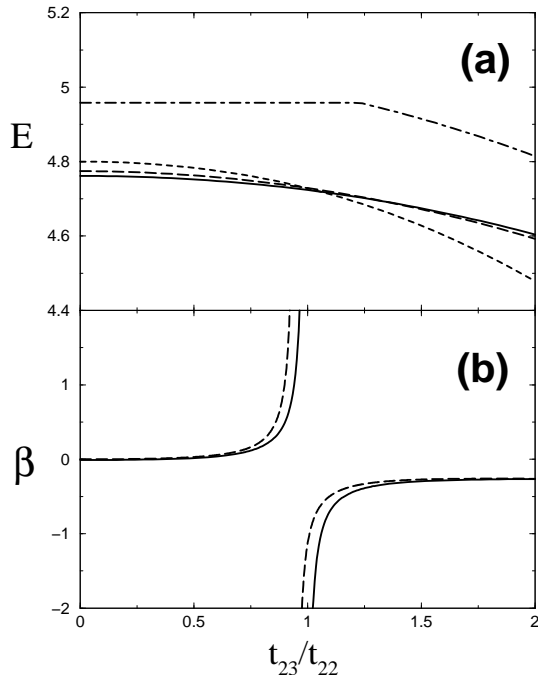


FIG. 4. Exact diagonalization results for a two-site cluster. a) Lowest energy levels in units of eV. Note the large gap between the three lowest levels (solid line: $S=0$; long-dashed line: $S=1$; short-dashed line: $S=2$) and the next one (dashed-dotted line). b) Relative biquadratic interaction β as a function of t_{23}/t_{22} for typical parameters ($t_{22} = .3$ eV, $\Delta = .3$ eV, $U = 6$ eV, $J_H = U/5$). Solid line: exact result; dashed line: perturbation result.

As stated above, the spin couplings are related to the energy levels of the two spin 1 system as a function of the total spin. These energies can be numerically calculated exactly. For a two-site system with four electrons and three orbitals at each site, we have calculated exactly the 495 energy levels for various parameters. As long as Δ is not too small as compared to the largest hopping integral, the low-energy part of the spectrum consists of three levels with total spin $S = 0$, $S = 1$ and $S = 2$ respectively (Fig. 4a). So the low energy effective Hamiltonian is indeed a spin 1 model. From the lowest energies E_S for total spin $S = 0, 1$ and 2 , we have extracted J_1 and J_2 . Our numerical results are in good agreement with the perturbation theory. In particular, we find a transition from antiferromagnetic to ferromagnetic J_1 as a function of $\alpha = t_{23}/t_{22}$, and a sharp increase in β in the same region. This transition corresponds to the crossings in Fig. 4a. The exact numerical results for β as function of α for typical parameters are also plotted in Fig. 4b. Except for the precise value of α for which β diverges, the essential features found in the exact nu-

merical calculations are the same as in the perturbation theory. Let us note that the numerical results do not depend qualitatively on the details of the parameters as long as the fundamental processes are present: There is always a value of t_{23}/t_{22} around 1 at which β diverges. So although the simplified model presented here in order to have compact expressions for the fourth order perturbation results ($t_{11} = t_{12} = t_{13} = 0$, $t_{33} = t_{22}$) is not exactly realized in LiVGe_2O_6 , we have checked numerically that the appropriate extension gives the same behaviour.

The relative value of the biquadratic interaction β depends sensitively on the ratio of the hopping integrals, but not on their magnitude. Application of a pressure on the system, if it is uniformly added, may not change the ratio of these hopping integrals, hence the biquadratic interaction sensitively. A uniaxial pressure, on the other hand, may change the hopping integrals in different proportions, and could dramatically affect the magnetic properties of the system. This possibility would be worth investigating in the case of LiVGe_2O_6 .

Finally, let us put these results in perspective. Although this mechanism would apply in any dimension, there is something very special about 1D. In higher dimension, fourth-order perturbation theory produces other types of four-spin interactions involving spins at four different sites. However, in 1D these processes do not appear as long as the hopping to further neighbours can be neglected, which usually is the case. So this mechanism is somehow specific to 1D. This might be the reason why it was overlooked in early attempts at producing strong biquadratic interactions because they were done before Haldane's conjecture and were more concerned with 3D magnets.

This mechanism is also somehow related to the problem of orbital degeneracy. It is well known that orbital degeneracy leads to a Hamiltonian which is not purely Heisenberg, but involves a pseudo-spin for the orbital degrees of freedom [9]. For spin 1/2 systems, for which most of the work has been done, the bilinear interaction is the only candidate - higher order terms do not appear because they can be rewritten in terms of the bilinear interaction - and the situation is a clear cut: Either the orbitals do not play a role, and the Hamiltonian is purely Heisenberg, or they do, and the Hamiltonian is a spin-orbital model. For spin 1 systems, we showed that, on going from a Heisenberg to a spin-orbital model by pulling down an empty orbital, there is an intermediate region where the Hamiltonian is still a pure spin Hamiltonian, but with a more general interaction than just bilinear due to a non-trivial level crossing (Fig. 4a). This simple idea should be useful in other contexts as well in looking for general spin Hamiltonians. In that respect, we hope that the present results will encourage quantum chemists to look more closely at exchange in situations where orbitals are quasi-degenerate. Quantum chemistry has proven to be able to reproduce very accurately on the basis of *ab initio* calculations the values of the exchange integrals of several systems. It should thus be possible along the

same lines to specify more precisely the conditions under which the mechanism proposed in this paper will apply.

In conclusion, we have provided a simple but efficient mechanism to produce significant biquadratic interactions in spin 1 chains. It is our hope that these ideas will ultimately lead to an experimental investigation of the fascinating phase diagram of the general spin 1 model in one dimension.

NOTE: After completion of this project, we became aware of a paper by Bhatt and Yang [R. N. Bhatt and K. Yang, J. Appl. Phys. **83**, 7231 (1998)] who considered a similar problem in the context of random antiferromagnetic spin chains. Their model is slightly different from ours (they consider the case of N degenerate orbitals with a simplified interaction), and they restrict themselves to a perturbation calculation, but our results are qualitatively consistent with theirs.

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